

## PATENT ABSTRACTS OF JAPAN

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G03F 7/027  
G03F 7/075  
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(54) POSITIVE TYPE PHOTSENSITIVE RESIN COMPOSITION AND SEMICONDUCTOR DEVICE USING SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a positive type photosensitive resin composition giving a film which is light-colored after curing and is less liable to discolor even in a heat treating process after curing.

SOLUTION: The positive type photosensitive resin composition comprises 100 pts.wt. polyamide (A), 1-100 pts.wt. photosensitive diazoquinone compound (B) and 1-20 pts.wt. hindered phenol antioxidant (C). The semiconductor device is produced using the photosensitive resin composition.

### LEGAL STATUS

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the examiner's decision of rejection or  
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

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decision of rejection]

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decision of rejection]

[Date of extinction of right]

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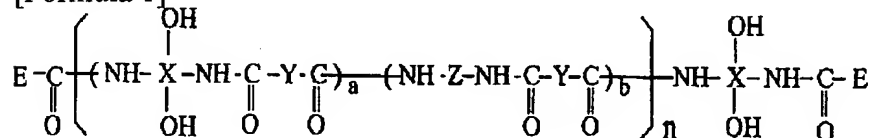
3. In the drawings, any words are not translated.

## CLAIMS

## [Claim(s)]

[Claim 1] a general formula -- (-- I --) -- being shown -- having -- a polyamide -- (-- A --) -- 100 -- weight -- the section -- photosensitivity -- diazo one -- a quinone -- a compound -- (-- B --) -- one - 100 - weight -- the section -- hindered one -- \*\* -- phenolic acid ---izing -- an inhibitor -- (-- C --) -- one - 20 -- weight -- the section -- from -- becoming -- things -- the feature -- \*\* -- carrying out -- a positive type -- a photopolymer -- a constituent .

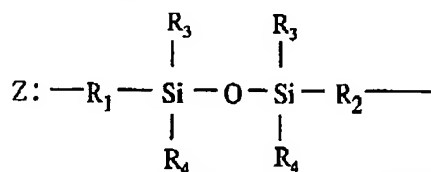
## [Formula 1]



式中 X:4価の環式化合物基

Y:2価の環式化合物基

(I)



(R<sub>1</sub>, R<sub>2</sub>:2価の有機基、R<sub>3</sub>, R<sub>4</sub>:1価の有機基)

E:アルケニル基又はアルキニル基を少なくとも1個を有する  
脂肪族又は環式化合物基

a, b はモル分率を示し、a+b=100モル%

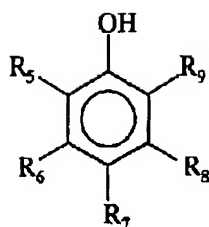
a=60.0~100.0モル%

b=0~40.0モル%

n=2~500

[Claim 2] A positive type photopolymer constituent according to claim 1 this whose hindered \*\* phenolic acid-ized inhibitor (C) is the structure chosen from what is shown by general formula (II), (III), (IV), and (V).

## [Formula 2]



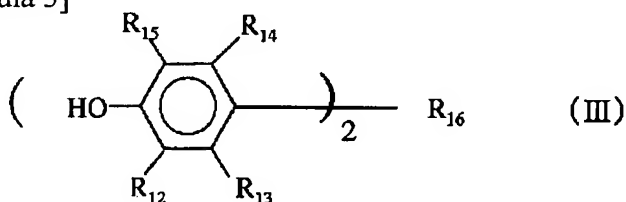
(II)

R<sub>5</sub> : t-ブチル基R<sub>6</sub>、R<sub>8</sub> : 水素原子又はアルキル基、R<sub>7</sub> : 水素原子又はアルキル基又はアルコキシ基、

ヒドロキシアルキル基又はジアルキルアミノアルキル基

又はヒドロキシ基又は-CH<sub>2</sub>CH<sub>2</sub>COOR<sub>10</sub>基又は-CH<sub>2</sub>CH(COOR<sub>11</sub>)<sub>2</sub> 基(R<sub>10</sub>、R<sub>11</sub>はアルキル基を表す)R<sub>9</sub> : 水素原子又はアルキル基

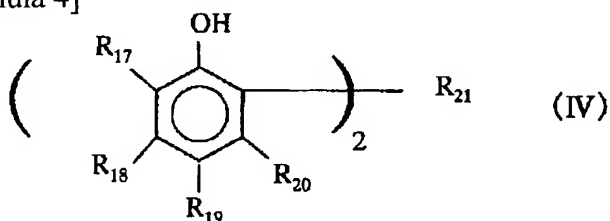
[Formula 3]



(III)

R<sub>12</sub> : t-ブチル基R<sub>13</sub>、R<sub>14</sub>、R<sub>15</sub> : 水素原子又はアルキル基R<sub>16</sub> : アルキレン基又は-S-又は-CH<sub>2</sub>-S-CH<sub>2</sub>又は-CH<sub>2</sub>CH<sub>2</sub>COO-R<sub>18</sub>-OOCCH<sub>2</sub>CH<sub>2</sub>-又は(R<sub>18</sub>は-(CH<sub>2</sub>)<sub>6</sub>、-CH<sub>2</sub>CH<sub>2</sub>-S-CH<sub>2</sub>CH<sub>2</sub>--CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-等を表す) 又は-CH<sub>2</sub>CH<sub>2</sub>CONH-(CH<sub>2</sub>)<sub>6</sub>-NHCOCH<sub>2</sub>CH<sub>2</sub>-

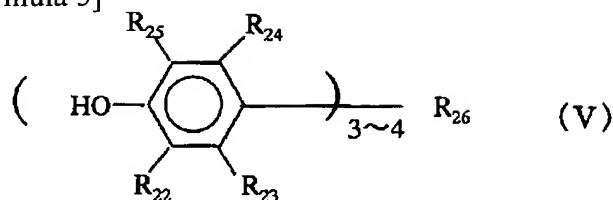
[Formula 4]



(IV)

R<sub>17</sub> : t-ブチル基又はシクロヘキシル基又は  
メチルシクロヘキシル基R<sub>18</sub>、R<sub>19</sub>、R<sub>20</sub> : 水素原子又はアルキル基R<sub>21</sub> : アルキレン基又は-S-又はテレフタル酸エステル

[Formula 5]



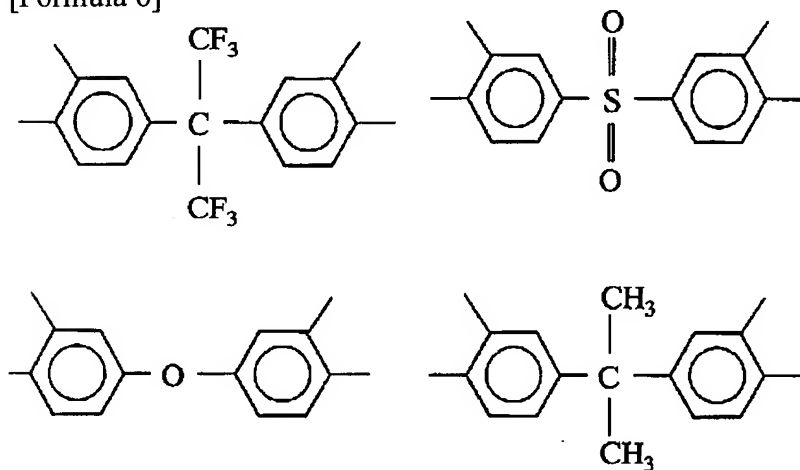
$R_{22}$  : t-ブチル基

$R_{23}$ 、 $R_{24}$ 、 $R_{25}$  : 水素原子又はアルキル基

$R_{26}$  : アルキル基の誘導体又はベンゼンからなる誘導体  
又はイソシアルレート基からなる誘導体又は  
プロピオネート基からなる誘導体

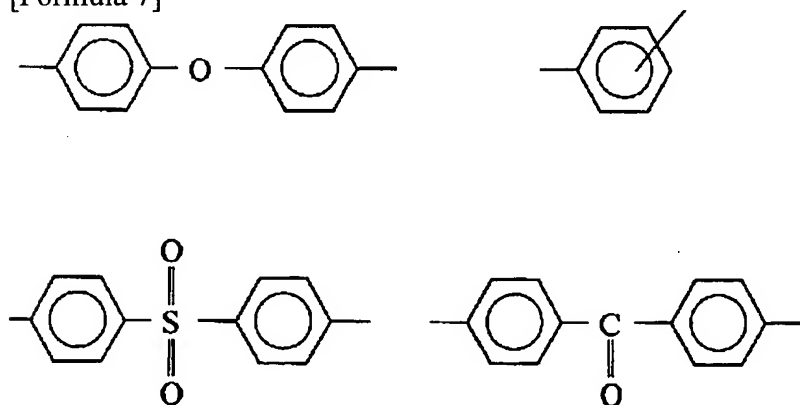
[Claim 3] A positive type photopolymer constituent according to claim 1 or 2 with which it comes to choose X in a polyamide of a general formula (I) out of the following.

[Formula 6]



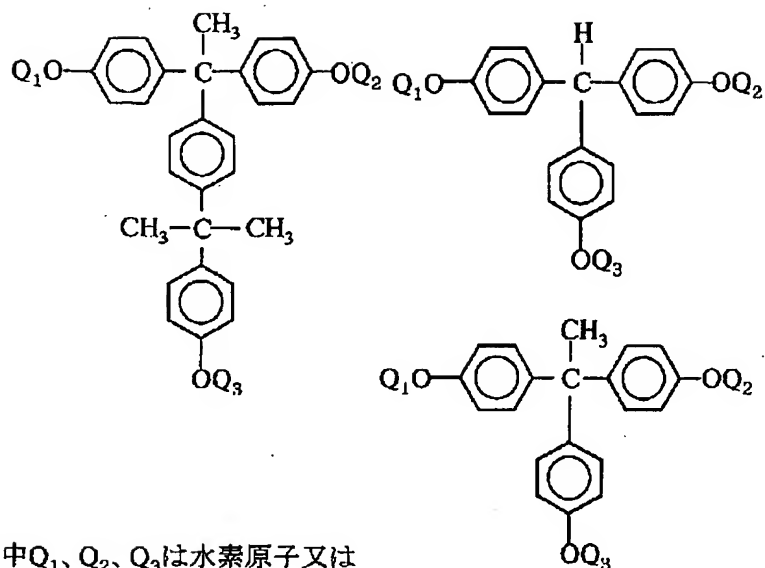
[Claim 4] A positive type photopolymer constituent according to claim 1, 2, or 3 with which it comes to choose Y in a polyamide of a general formula (I) out of the following.

[Formula 7]

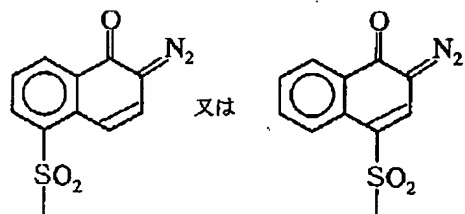


[Claim 5] A positive type photopolymer constituent according to claim 1 or 2 with which it comes to choose this photosensitive diazo quinone compound (B) out of the following.

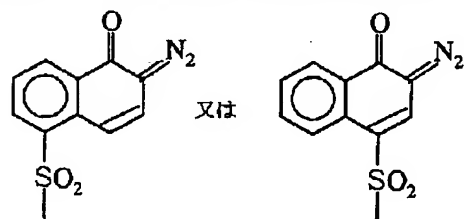
[Formula 8]



(式中 $Q_1$ 、 $Q_2$ 、 $Q_3$ は水素原子又は



を意味し、 $Q_1$ 、 $Q_2$ 、 $Q_3$ の少なくとも1つは、



を意味する。)

[Claim 6] A semiconductor device manufactured using a positive type photopolymer constituent according to claim 1 to 5.

[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

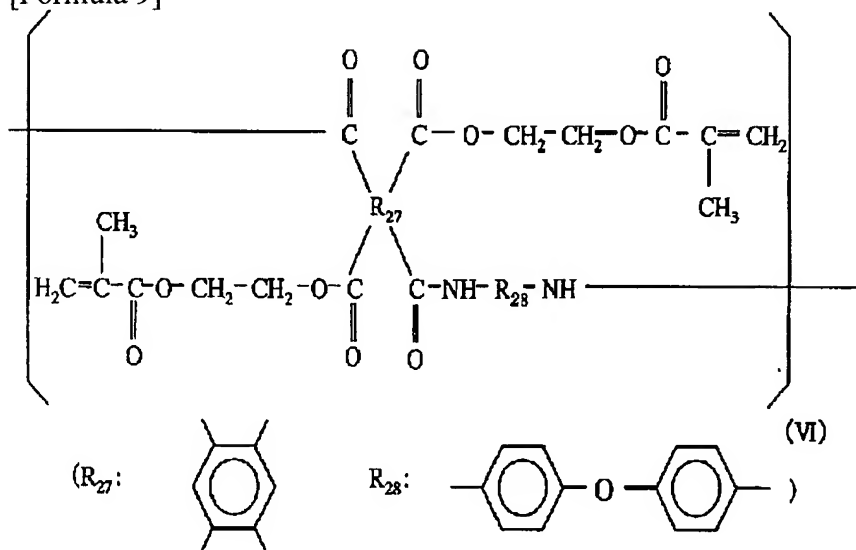
[The technical field to which invention belongs] The color of this invention of the film after hardening is light, and it is related with a positive type photopolymer constituent with little discoloration also in the heat treatment process after hardening.

[0002]

[Description of the Prior Art] Although the polyimide resin which has from the former the electrical property in which thermal resistance was excellent in and excelled as the surface-protection film of a semiconductor device and an interlayer insulation film, a mechanical characteristic, etc. is used, there is a demand of the remarkable improvement in heat-resistant cycle nature, heat-resistant shock nature, etc. by the shift to the surface mount by high integration of a semiconductor device, enlargement, thin-shape-izing of a package, a miniaturization, and the solder reflow etc., and the resin of high performance has come to be needed further in recent years. The photosensitive polyimide resin with which the technology which gives photosensitivity to polyimide resin itself attracts attention recently, for example, is shown in the following formula (VI) on the other hand is mentioned.

[0003]

[Formula 9]



[0004] When this is used, a part of pattern creation process can be simplified, there is an effect of process compaction, but since solvents, such as a N-methyl-2-pyrrolidone, are needed in the case of development, a problem is in safety and handling nature. Then, the photopolymer of the positive type which can do development in an alkali aqueous solution is developed recently. For example, the positive type photopolymer which consists of a poly benzo oxazole precursor and a diazo quinone compound in



JP,1-46862,B is indicated. This has high thermal resistance, the outstanding electrical property, and micro-processing nature, and has not only the object for wafer coats but the possibility as resin for layer insulation. Although the diazo quinone compound of the unexposed section is insoluble in an alkali aqueous solution, when the development mechanism of the photopolymer of this positive type is exposed, a diazo quinone compound becomes meltable in a lifting and an alkali aqueous solution about a chemical change. Creation of the paint film pattern of only the unexposed section is attained by using the soluble difference of this exposure section and the unexposed section, and carrying out dissolution clearance of the exposure section.

[0005] It is the general process which is changed into the film which the positive type photopolymer shown in this JP,1-46862,B heat-treated, carried out the ring closure at the temperature of about 300-400 degrees C after development (hardening), and was excellent in thermal stability. However, when this hardening is performed, poly benzo oxazole resin and a diazo quinone compound decompose and oxidize, and a film's say [ it / that it discolors ] black and are problematic. Moreover, in the manufacture process of a semiconductor, various heat treatments are performed also after the process of polyimide. For example, in the case of LOC structure, a leadframe with a LOC tape is stuck to a chip by pressure at a 350-450-degree C elevated temperature. The poly benzo oxazole resin which carried out the coat to the chip is also discolored black in that case. Discoloration generates poor recognition at the time of wire bonding performed after that. Then, the color of the film after hardening is light, and a positive type photopolymer constituent with little discoloration is desired also in the heat treatment process after hardening.

[0006]

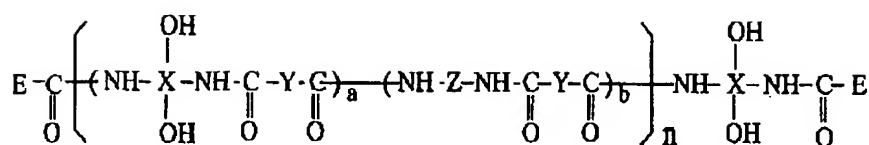
[Problem(s) to be Solved by the Invention] The color of the film after hardening is light, and is related with a positive type photopolymer constituent with little discoloration also in the heat treatment process after hardening.

[0007]

[Means for Solving the Problem] a general formula -- (-- I --) -- being shown -- having -- a polyamide -- (-- A --) -- 100 -- weight -- the section -- photosensitivity -- diazo one -- a quinone -- a compound -- (-- B --) -- one - 100 -- weight -- the section -- hindered ones -- \*\* -- phenolic acid ---izing -- an inhibitor -- (-- C --) -- one - 20 -- weight -- the section -- from -- becoming -- a positive type -- a photopolymer -- a constituent -- it is . Moreover, it is the semiconductor device manufactured using this positive type photopolymer constituent.

[0008]

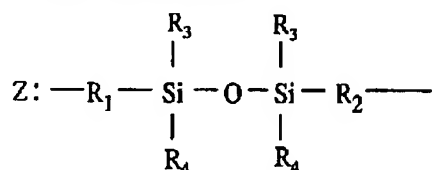
[Formula 10]



式中 X:4価の環式化合物基

(I)

Y:2価の環式化合物基



(R<sub>1</sub>, R<sub>2</sub>:2価の有機基、R<sub>3</sub>, R<sub>4</sub>:1価の有機基)

E:アルケニル基又はアルキニル基を少なくとも1個を有する  
脂肪族又は環式化合物基

a、b はモル分率を示し、a+b=100モル%

a=60.0~100.0モル%

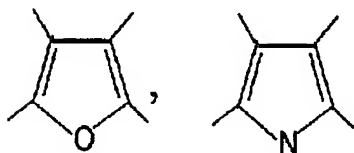
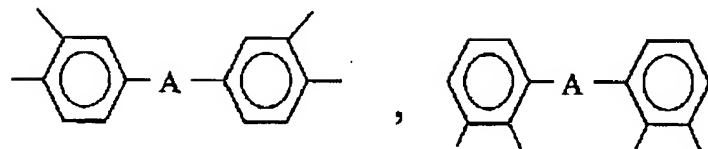
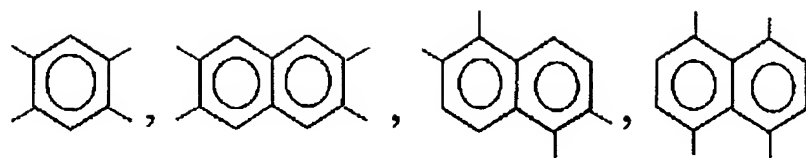
b=0~40.0モル%

n=2~500

[0009]

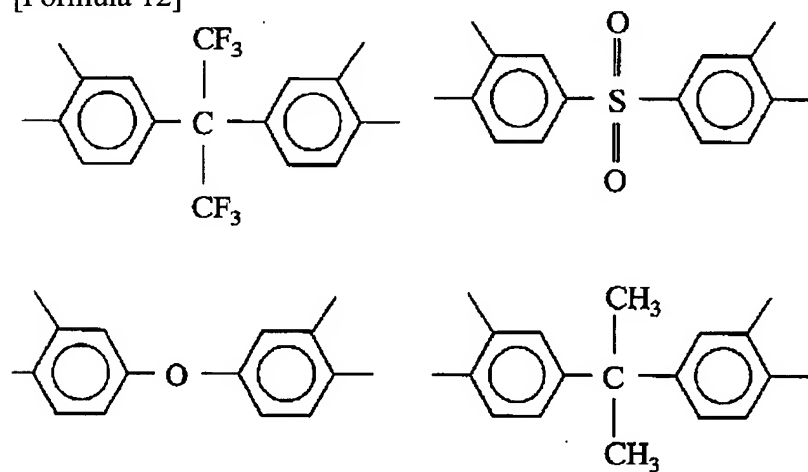
[Embodiment of the Invention] The polyamide of a formula (I) is compounded from the diamine which has the structure of X, the dicarboxylic acid which has the structure of Y, and the carboxylic-acid derivative which has the structure of E further, if this polyamide is heated at about 300-400 degrees C, the dehydration ring closure of it will be carried out, and it changes to heat resistant resin called the poly benzo oxazole. X of the polyamide (I) of this invention -- for example [0010]

[Formula 11]

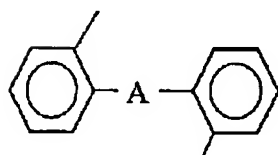
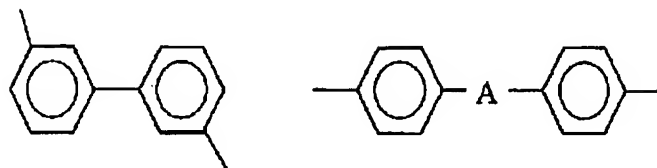
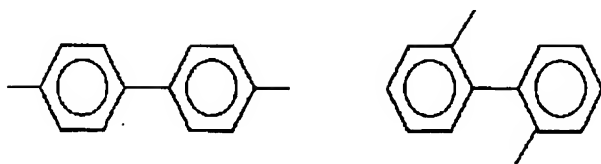
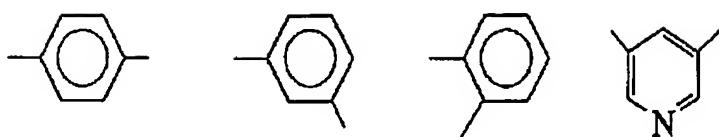


(式中A:  $-\text{CH}_2-$ ,  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{SO}_2-$ ,  $-\text{CO}-$ ,  
 $-\text{NHCO}-$ ,  $-\text{C}(\text{CF}_3)_2-$ )

[0011] \*\*\*\*\* -- although -- it is not limited to these. A thing especially desirable in this, [0012]  
 [Formula 12]

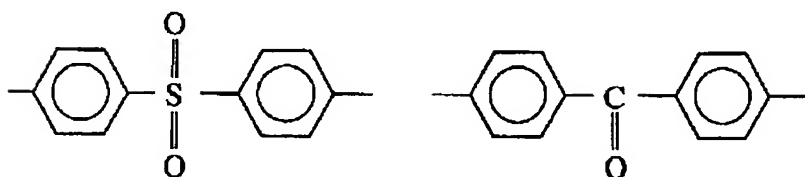
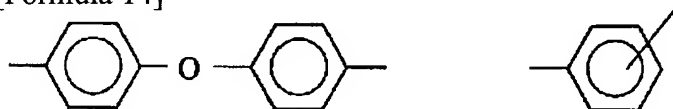


[0013] It is chosen more. Y of \*\*\*\* (I) -- for example [0014]  
 [Formula 13]



(式中A:  $-\text{CH}_2-$ ,  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{SO}_2-$ ,  $-\text{CO}-$ ,  
 $-\text{NHCO}-$ ,  $-\text{C}(\text{CF}_3)_2-$ )

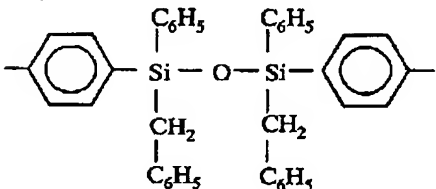
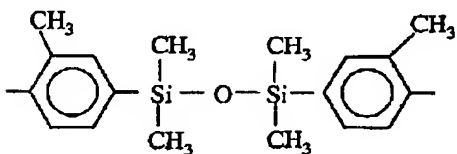
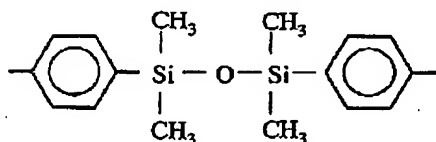
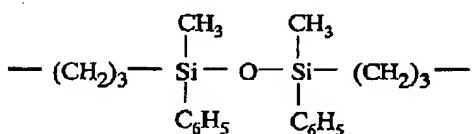
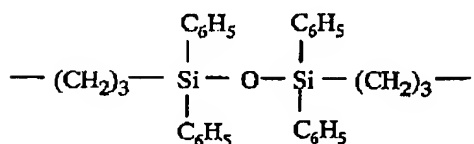
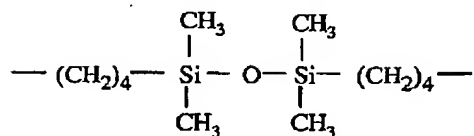
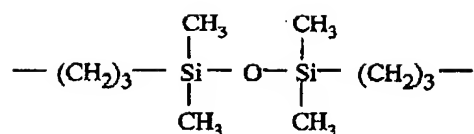
[0015] \*\*\*\*\* -- although -- it is not limited to these. A thing especially desirable in these, [0016]  
 [Formula 14]



[0017] It is chosen more. After E of \*\*\*\* (I) making the diamine which has the structure of the dicarboxylic acid derivative and X which have the structure of Y react and compounding a polyamide, Although the carboxylic-acid derivative which has an alkenyl radical or at least one alkynyl group for the end amino group is made to react, end closure is performed and 5-norbornene -2, 3-dicarboxylic acid anhydride, a maleic anhydride, etc. are mentioned as a carboxylic-acid derivative 5-norbornene -2 and 3-dicarboxylic acid anhydride are especially desirable. furthermore, Z of a formula (I) -- for example

[0018]

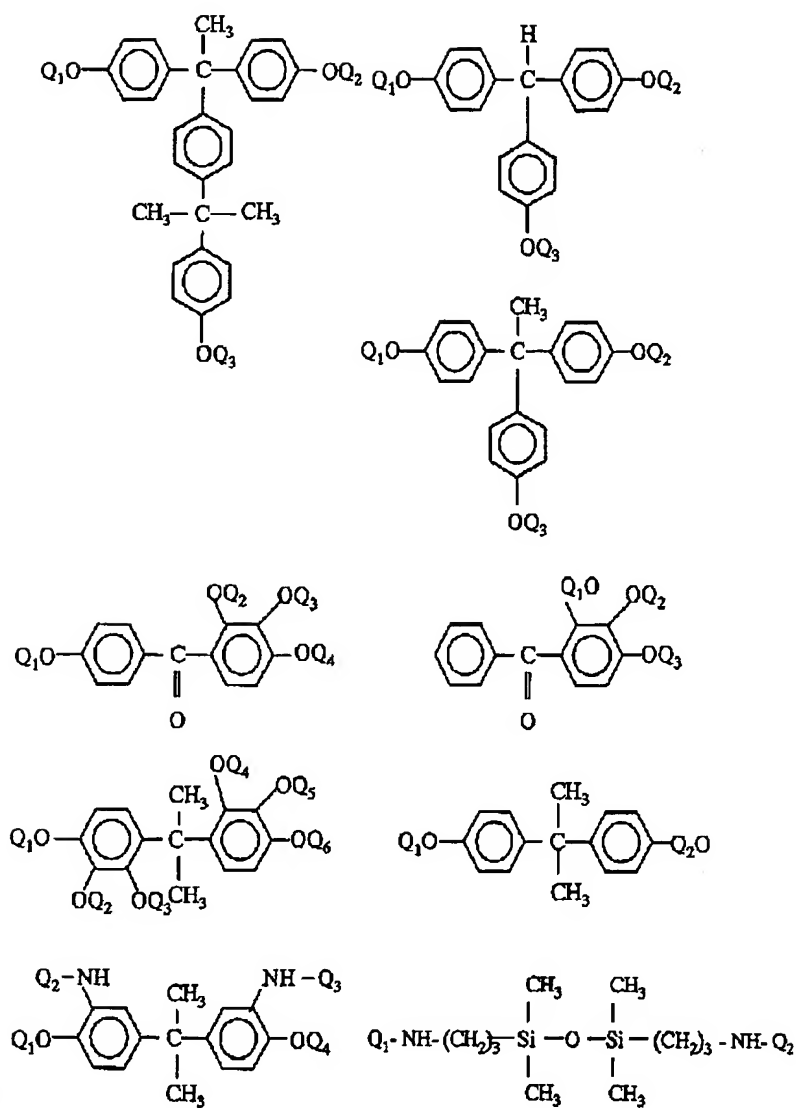
[Formula 15]



[0019] \*\*\*\*\* -- although -- it is not limited to these. Although Z of a formula (I) is used when further more high adhesion is required, the operating rate b is to a maximum of 40-mol %. If 40-mol % is exceeded, the solubility of resin will fall extremely, the development remainder (Society for Cutting Up Men) occurs, and pattern processing cannot be performed. In addition, in an activity of these X, Y, E, and Z, it does not matter even if it is one kind, respectively and is two or more kinds of mixture.

[0020] The photosensitive diazo quinone compound used by this invention is a compound which has 1 and 2-benzoquinone diazido or 1, and 2-naphthoquinonediazide structure, and are U.S. Pat. No. 2,772,972, No. 2,797,213, and the matter well-known No. 3,669,658. For example, the following are mentioned.

[0021]

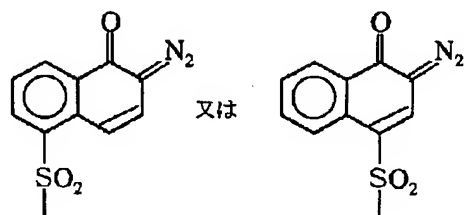


[Formula 16]

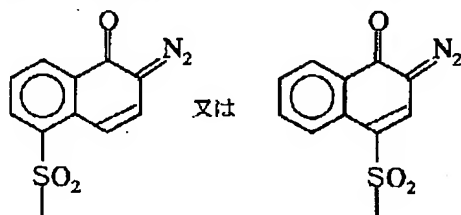
[0022]

[Formula 17]

(式中 $Q_1$ 、 $Q_2$ 、 $Q_3$ 、 $Q_4$ 、 $Q_5$ 、 $Q_6$  は水素原子又は



を意味し、 $Q_1$ 、 $Q_2$ 、 $Q_3$ 、 $Q_4$ 、 $Q_5$ 、 $Q_6$ の少なくとも1つは、

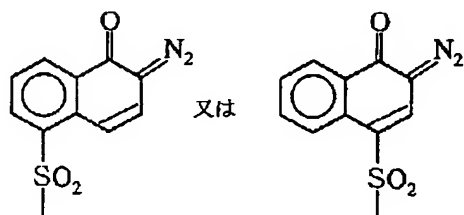
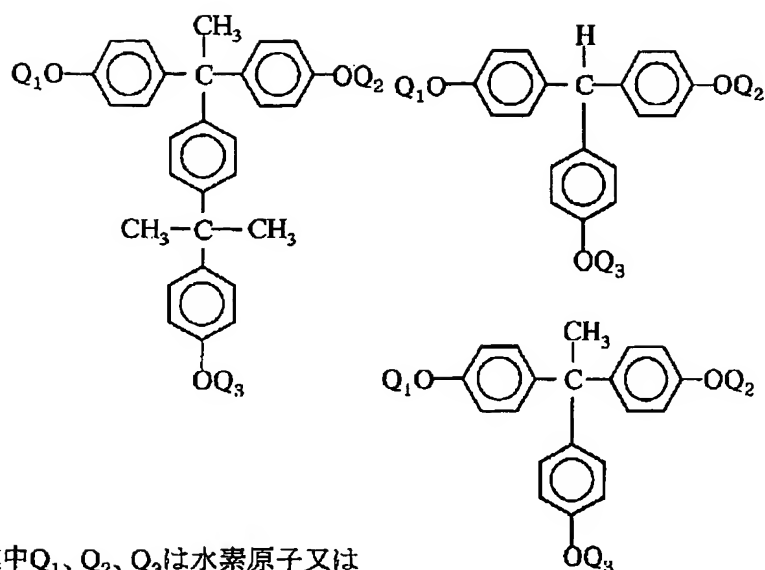


を意味する。)

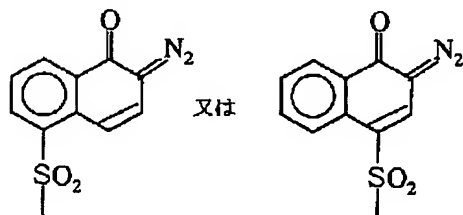
[0023] The following are desirable especially in these.

[0024]

[Formula 18]



を意味し、 $Q_1$ 、 $Q_2$ 、 $Q_3$ の少なくとも1つは、



を意味する。)

[0025] If the loadings to the polyamide (A) of a photosensitive diazo quinone compound (B) have the poor patterning nature of resin if the 1 - 100 weight section is desirable and loadings are under 1 weight section, and they exceed the 100 weight sections conversely to the polyamide 100 weight section, the tension pace of expansion of a film will fall remarkably.

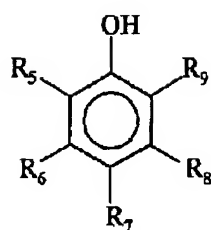
[0026] In order to raise a sensitization property as occasion demands, a dihydropyridine derivative can be added to the positive type photopolymer constituent of this invention. As a dihydropyridine derivative, for example 2, the 6-dimethyl -3, 5-diacetyl-4-(2'-nitrophenyl)-1, a 4-dihydropyridine, 4-(2'-nitrophenyl)-2, the 6-dimethyl -3, 5-JIKARUBO ethoxy -1, a 4-dihydropyridine, 4-(2' and 4'-dinitrophenyl)-2, the 6-dimethyl -3, 5-JIKARUBO methoxy -1, a 4-dihydropyridine, etc. can be mentioned.

[0027] It makes it indispensable to use a hindered \*\* phenolic acid-ized inhibitor further in the positive type photopolymer constituent of this invention. It is the compound which has the structure expressed with general formula (II)- (V) to intramolecular as a hindered \*\* phenolic acid-ized inhibitor which can be used for this invention.

[0028]

[Formula 19]





(II)

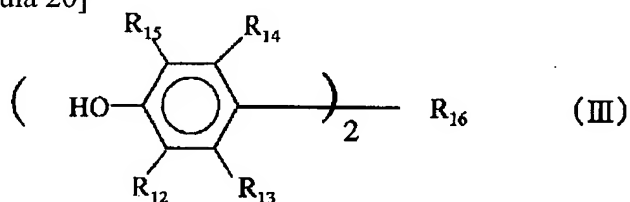
R<sub>5</sub> : t-ブチル基R<sub>6</sub>、R<sub>8</sub> : 水素原子又はアルキル基、R<sub>7</sub> : 水素原子又はアルキル基又はアルコキシ基、

ヒドロキシアルキル基又はジアルキルアミノアルキル基

又はヒドロキシ基又は-CH<sub>2</sub>CH<sub>2</sub>COOR<sub>10</sub>基又は-CH<sub>2</sub>CH(COOR<sub>11</sub>)<sub>2</sub> 基(R<sub>10</sub>、R<sub>11</sub>はアルキル基を表す)R<sub>9</sub> : 水素原子又はアルキル基

[0029]

[Formula 20]

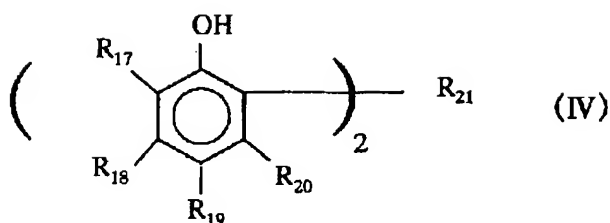


(III)

R<sub>12</sub> : t-ブチル基R<sub>13</sub>、R<sub>14</sub>、R<sub>15</sub> : 水素原子又はアルキル基R<sub>16</sub> : アルキレン基又は-S-又は-CH<sub>2</sub>-S-CH<sub>2</sub>又は-CH<sub>2</sub>CH<sub>2</sub>COO-R<sub>18</sub>-OOCCH<sub>2</sub>CH<sub>2</sub>-又は(R<sub>18</sub>は-(CH<sub>2</sub>)<sub>6</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-S-CH<sub>2</sub>CH<sub>2</sub>--CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-等を表す) 又は-CH<sub>2</sub>CH<sub>2</sub>CONH-(CH<sub>2</sub>)<sub>6</sub>-NHCOCH<sub>2</sub>CH<sub>2</sub>-

[0030]

[Formula 21]



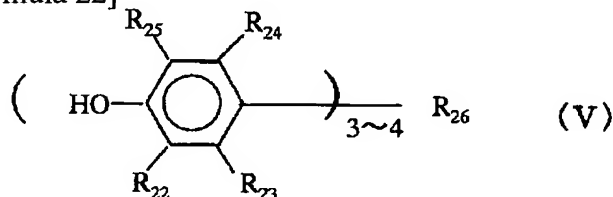
$R_{17}$ : t-ブチル基又はシクロヘキシル基又は  
メチルシクロヘキシル基

$R_{18}$ 、 $R_{19}$ 、 $R_{20}$ : 水素原子又はアルキル基

$R_{21}$ : アルキレン基又は-S-又はテレフタル酸エステル

[0031]

[Formula 22]



$R_{22}$ : t-ブチル基

$R_{23}$ 、 $R_{24}$ 、 $R_{25}$ : 水素原子又はアルキル基

$R_{26}$ : アルキル基の誘導体又はベンゼンからなる誘導体  
又はイソシアルレート基からなる誘導体又は  
プロピオネート基からなる誘導体

[0032] The example of the hindered \*\* phenolic acid-ized inhibitor which can be used for this invention About a general formula (II), for example, 2,6-di-tert-butyl-4-methylphenol, 2,5-di-tert-butylhydroquinone, octadecyl-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate, Iso octyl-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate etc. about a general formula (III) again for example A - methylenebis (2, 6-G t-butylphenol), and 4 and 4' 4, 4'-thio-screw (3-methyl-6-t-butylphenol), 4 and 4'-butylidenebis (3-methyl-6-t-butylphenol), A triethylene glycol-screw [3-(3-t-butyl-5-methyl-4-hydroxyphenyl) propionate], A 1,6-hexanediol-screw [3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate], A 2 and 2-thio-diethylene screw [3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate], N and N' hexa methylenebis (3 5 - G t-butyl-4-hydroxy-hydronalium thinner MAMIDO) etc. -- moreover -- a general formula (IV) -- for example - methylenebis (4-methyl-6-t-butylphenol), and 2 and 2' 2, 2'-methylenebis (4-ethyl-6-t-butylphenol) etc. -- moreover -- a general formula (V) -- for example Pentaerythrityl-tetrakis [3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate], Tris -(3, 5-G t-butyl-4-hydroxybenzyl)-Isocyanurate, 1 and 3, 5-trimethyl -2, 4, and 6-tris (3, 5-G t-butyl-4-hydroxybenzyl) benzene etc. is mentioned. Moreover, even if it uses it independently in these activities, it can be used with two or more kinds of mixture.

[0033] The loadings to the positive type photopolymer constituent of a hindered \*\* phenolic acid-ized inhibitor are 1 - 20 weight section to the (Polyamide A) 100 weight section. If loadings are under 1 weight section, the effect of discoloration-proof will not be acquired, and if 20 weight sections are exceeded, sensitivity will fall, a problem is in practicability, and it is not desirable.

[0034] In the positive type photopolymer constituent in this invention, additives, such as a leveling agent

and a silane coupling agent, can be added as occasion demands.

[0035] In this invention, these components are dissolved in a solvent, and it is used by making it the shape of a varnish. As a solvent, a N-methyl-2-pyrrolidone, gamma-butyrolactone, N,N-dimethylacetamide, dimethyl sulfoxide, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dibutyl ether, Propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, Propylene-glycol-monomethyl-ether acetate, methyl lactate, Ethyl lactate, butyl lactate, methyl -1, 3-butylene-glycol acetate, 1, the 3-butylene-glycol-3-monomethyl ether, methyl pyruvate, pyruvic-acid ethyl, methyl-3-methoxy propionate, etc. are mentioned, and it may be independent, or you may mix and use.